LIGAND FIELD THEORY OF TRIGONALLY DISTORTED OCTAHEDRAL Ni^{2+} SALTS.

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ABSTRACT. Measurements of the magnetic susceptibility and anisotropy on single crystals of $NiSiF_6.6H_2O$ and $NiSnCl_6.6H_2O$ have been made in the temperature range 300° 90°K and the results are compared with the theoretical expressions. In both these crystals (which belong to the trigonal system with one ion in the unit cell) the anisotropic ligand field parameters as well as the zero field splitting are seen to be temperature dependent, the changes being more pronounced in the fluosilicate. The effect of covalency appears to be high in the chlorostannate.

INTRODUCTION

The hexahydrated fluosilicate and chlorostannate of Ni^{2+} belong to an interesting series of crystals for magnetic, optical, e.s.r. and other studies. The unit cell of the trigonal (rhombohedral) crystals contains only one molecule, the $Ni(H_2O)_6^{+2}$ octahedra being trigonally distorted along the 3-fold axis of the crystals, as evident from the *x*-ray analysis of the chlorostannate by Pauling (1930) and the recent neutron diffraction studies on the isomorphous ferrous fluosilicate by Hamilton (1962). The Ni^{2+} ion is thus under a predominantly octahedral field with a small superposed trigonal component. The ground level of the ion under a cubic field is an orbital singlet $^3A_{2g}$, which is split up to a small extent by the combined action of the spin orbit coupling and the non-cubic component of the field into a doublet and a singlet. The magnitude of the separation between these levels, the zero field splitting D, has been measured from the resonance spectra (Holden, Kittel and Yager, 1949; Penrose and Stevens, 1950). However, the sign of D cannot be determined from these data and has to be deduced from magnetic susceptibility measurements, as discussed later.

Only the mean susceptibility data for the fluosilicate in the temperature range 290°–1.54°K have so far been reported (Haseda and Date, 1958) which are not enough for evaluating all the theoretical parameters uniquely. In the present paper we have measured the magnetic anisotropy as well as the principal susceptibilities in the range 300°-90°K. The study of magnetic anisotropy is of special advantage here, as it is a sensitive function of D (vide infra). Results on the isomorphous salt, $NiSnCl_6$, $6H_2O$, have also been discussed.

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EXPERIMENTAL

Nickel fluosilicate was prepared from nickel carbonate (Schering's Co-free quality) and neutralized with hydrofluoric acid. Zinc fluosilicate (which was required for the diamagnetic correction of the susceptibilities) was prepared in a similar manner. Nickel chlorostannate was prepared from $NiCl_2 6H_2O$ and $SnCl_4$ in moderately concentrated hydrochloric acid solution. The fairly large single crystals obtained on crystallization from slightly acid solutions were checked under the polarising microscope. $NiSiF_6 \cdot 6H_2O$ crystals were ground into cylinders about the axis of suspension to eliminate shape effects on the magnetic anisotropy. $NiSnCl_6 \cdot 6H_2O$ is very deliquescent and had to be coated with collodion after mounting in the sample holder. Grinding of these crystals was avoided by choosing only those that had as nearly a regular polygonal cross-section as possible about the axis of suspension, so that the shape effects were minimized (Majumdar, 1962).

The magnetic anisotropy was measured in a torsion balance with quartz fibre suspension described in detail by Majumdar and Datta (1965), from which the values of the anisotropy $\Delta\chi$ in the horizontal plane could be directly obtained. For the measurement of the principal anisotropy $(\chi_{\parallel} - \chi_{\perp})$ (the susceptibility along the trigonal axis, $\chi_{\parallel}$, was found to be greater than that normal to this axis, $\chi_{\perp}$, for both the salts studied here) the crystal was oriented with a $\{1\bar{1}0\}$ face horizontal. In order to check if any anisotropy appeared in the plane of trigonal symmetry at low temperatures, the crytals was mounted with the [111] axis vertical. There was no measurable anisotropy down to 90°K, showing that the unlike cobalt (Majumdar and Datta, 1965), manganese (Tsujikawa, and Couture, 1955) and copper (Majumdar, unpublished) hexa-aquo fluosilicates, the uniaxial symmetry of the crystal is retained in both the salts in the range of temperature studied.

A sensitive Curie type of torsion balance was used for the measurement of susceptibility (Bose *et al.*, 1963) and one of the principal susceptibilities of the crystal, e.g., $\chi_{\perp}$ or the mean susceptibility of the powdered crystal was measured from 300° to 90°K with its help Measurement of the mean susceptibility was not possible for the chlorostannate because of the obvious difficulty of powdering and packing the highly deliquescent crystals in an ampoule. The susceptibility values for $NiSiF_6 \cdot 6H_2O$ were corrected for diamagnetism from the measurements on the isomorphous zinc fluosilicate for which $K_{\parallel}$ and $K_{\perp}$ were found to be -136.4 and -135.5 in the usual 10^{-6} e.m. units per mole, respectively. For the chlorostannate no isomorphous diamagnetic salt containing $SnCl_6^{2-}$ could be prepared, and the necessary corrections were applied using standard tables*, $\bar{\chi}$ being calculated to be -252.

*Tables de constantes et donénes numériques, 1957, Edited by G. Foex *et al.*, Vol. 7 "Diamagnetismé et Paramagnetismé".

From the corrected susceptibility values the principal and mean effective moments μ_i ($i = \parallel$ or $\perp$ to the trigonal axis) and μ, respectively, were calculated

$$\mu_i^2 = \frac{3k}{N\beta^2}\chi_i \cdot T = 7.995\chi_i T$$

$$\mu^2 = \tfrac{1}{3}(\mu_\parallel^2 + 2\mu_\perp^2)$$

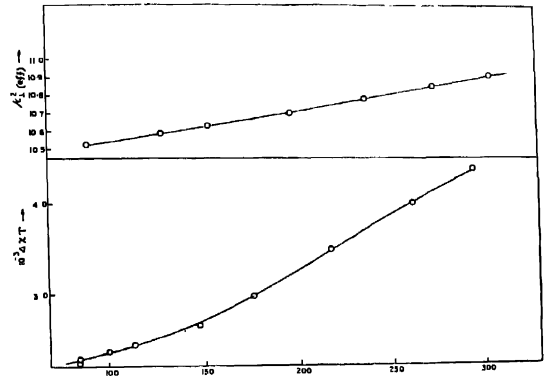

Fig. 1. $NiSiF_6.6H_2O$. Lower curve—magnetic anisotropy, $(\chi_\parallel - \chi_\perp)$, plotted as $T(\chi_\parallel - \chi_\perp)$; Upper curve—squares of the principal moments, $\mu_\perp{}^2$ (eff.)

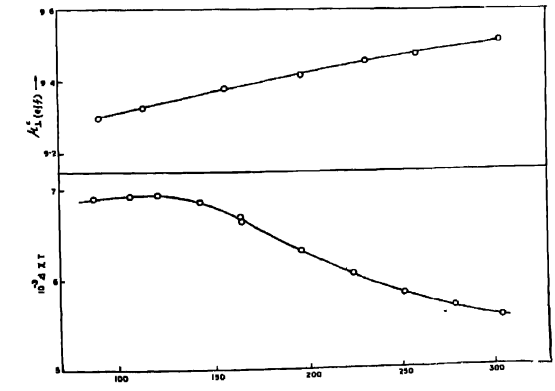

Fig. 2. $NiSnCl_6.6H_2O$ Lower curve—magnetic anisotropy, $(\chi_\parallel - \chi_\perp)$, plotted as $T(\chi_\parallel - \chi_\perp)$, Upper curve—squares of the principal moments, $\mu_\perp{}^2$ (eff.)

using the relationship (χ_i being identical with the ionic susceptibility K_i in the present case) The experimental data for the anisotropy and the susceptibility (or the squares of the principal effective moment μ^2) are shown in figure 1 for the fluosilicate and in figure 2 for the chlorostannate. Graphically interpolated values at regular intervals of temperature are shown in Tables I and II for convenience of comparison with the calculated values. The accuracy of the results is estimated to be $\pm 0.5\%$.

TABLE I

Magnetic anisotropy and susceptibility of $NiSiF_6 \cdot 6H_2O$
(interpolated values)

Temp. °K	$10^6 K_\perp$	$10^6(K_\parallel - K_\perp)$	$10^6\bar{K}$
300	4,530	14.82	4,530
280	4,830	15.00	4,840
260	5,190	15 21	5,200
240	5,610	15.46	5,610
220	6,090	15.80	6,100
200	6,680	16.23	6,680
180	7,400	16 70	7,420
160	8,300	17 40	8,310
140	9,450	18 57	9,460
120	9,990	20.54	10,100
100	13,170	23 63	13,180
90	14,610	25.62	14,610

TABLE II

Magnetic anisotropy and susceptibility of $NiSnCl_6 \cdot 6H_2O$
(interpolated values)

Temp. °K	$10^6 K_\perp$	$10^6(K_\parallel - K_\perp)$	$10^6\bar{K}$
300	3,963	18 63	3,970
280	4,240	20.20	4,250
260	4,560	22.21	4,570
240	4,930	24.62	4,940
220	5,370	27.71	5,380
200	5,890	31.40	5,910
180	6,540	36.12	6,550
160	7,340	41.90	7,350
140	8,360	49.24	8,380
120	9,730	57.80	9,750
100	11,650	69.21	11,690
90	12,912	76.60	12,950

THEORY OF TRIGONALLY DISTORTED OCTAHEDRAL Ni^{2+} SALTS

Under an octahedral field of symmetry O_h the $3d^8$ ^3F ground state of the Ni^{2+} ion splits up into two triplets, $^3T_{2g}$ and $^3T_{1g}$, and a singlet $^3A_{2g}$ which lies lowest. The appropriate wave functions using the three-fold axis of the octahedron as the axis of quantization are (Bleaney and Stevens, 1953)

Wave functions	Representation	
$\frac{\sqrt{2}}{3}(\psi_3-\psi_{-3})-\frac{\sqrt{5}}{3}\psi_0$	A_{2g}	
$\frac{1}{\sqrt{2}}(\psi_3+\psi_{-3})$	T^0_{2g}	
$\sqrt{\frac{1}{6}}\psi_2-\sqrt{\frac{5}{6}}\psi_{-1}$	$T_{2g}{}^+$	
$\sqrt{\frac{5}{6}}\psi_1+\sqrt{\frac{1}{6}}\psi_{-2}$	T^-_{2g}	(1)
$\frac{2}{3}\psi_0+\frac{1}{3}\sqrt{\frac{5}{2}}(\psi_3-\psi_{-3})$	T^0_{1g}	
$\sqrt{\frac{5}{6}}\psi_2+\sqrt{\frac{1}{6}}\psi_{-1}$	T^+_{1g}	
$\sqrt{\frac{5}{6}}\psi_{-2}-\sqrt{\frac{1}{6}}\psi_1$	T^-_{1g}	

The potential for the cubic and trigonal fields may be written as

$$V = D'r^4\left[Y^0_4+\left(\frac{10}{7}\right)^{\frac{1}{2}}\left(Y^3_4-Y_4{}^{-3}\right)\right]+A'_2r^2Y^0_2+A_4'r^4Y^0_4 \quad \ldots \quad (2)$$

On applying the corresponding perturbations we arrive at the following wave functions :

$$\begin{aligned}
\phi_0 &= a_0|A_{2g}>+b_0|T^0_{1g}> \\
\phi_1 &= a_1|T^+_{2g}>+b_1|T^+_{1g}> \\
\phi_1' &= a_1|T^-_{2g}>+b_1|T^-_{1g}> \\
\phi_2 &= \quad |T^0_{2g}> \qquad \ldots \quad (3) \\
\phi_3 &= a_1|T^+_{1g}>-b_1|T^+_{2g}> \\
\phi'_3 &= a_1|T^-_{1g}>-b_1|T^-_{2g}> \\
\phi_4 &= a_0|T^0_{1g}>-b_0|A_{2g}>
\end{aligned}$$

with the corresponding energies (with appropriate subscripts) obtained by solving the secular determinant, given by

$$E_{0,4} = \frac{1}{2}\left[\left(-6Dq+\frac{3}{10}A_2+\frac{27}{2}A_4 \mp \left\{\left(18Dq+\frac{3}{10}A_2-\frac{1}{2}A_4\right)^2+\frac{4}{5}(3A_2-5A^2_4)^{\frac{1}{2}}\right\}^{\frac{1}{2}}\right]$$

$$E_{1,3} = \frac{1}{2}\left[\left(4Dq-\frac{9}{10}A_2-9A_4\right) \mp \left\{\left(8Dq+\frac{3}{5}A_2-8A_4\right)^2+\frac{1}{20}\left(3A_2-40A_4\right)^2\right\}^{\frac{1}{2}}\right]$$

$$E_2 = -2Dq+\frac{3}{2}A_2+\frac{9}{2}A_4 \qquad \ldots (4)$$

where the first and the second subscripts on E refer to the $-ve$ or $+ve$ sign appearing within the square brackets in (4). The coefficients in (3) are given by

$$a_0 = \frac{\frac{3}{\sqrt{5}}A_2-\sqrt{5}A_4}{E_0+12Dq-7A_4}b_0$$

$$a_0^2+b_0^2 = 1;$$

$$a_1 = \frac{\frac{3}{4\sqrt{5}}A_2-2\sqrt{5}A_4}{E_1+2Dq+\frac{3}{4}A_2+\frac{1}{2}A_4}b_1 \qquad \ldots (5)$$

$$a_1^2+b_1^2 = 1;$$

where the ligand field coefficients are given by

$$A_2 = -eA'_2\bar{r}^2\frac{\sqrt{5}}{21\sqrt{\pi}}$$

$$A_4 = -eA'_4\bar{r}^4\frac{1}{21\sqrt{\pi}} \qquad \ldots (6)$$

$$Dq = +eD'\bar{r}^4\frac{3}{28\sqrt{\pi}}$$

The trigonal field thus splits up the excited orbital triplets into a doublet and a singlet each, the ground level remaining orbitally non-degenerate. Since the excited orbital levels lie $\sim 10^4$ cm^{-1} higher up we can apply the spin Hamiltonian technique (Pryce, 1950) where we include the effect of spin-orbit interaction and the external magnetic field.

For $H//z$, axis of trigonal symmetry of the $Ni(H_2O)_6^{3+}$ complex, the spin Hamiltonian for the system is given by

$$H_s = D\{S_z^2 - \tfrac{1}{3}S(S+1)\} + \beta g_{\parallel} H_z S_z - \beta^2 \alpha_{\parallel} k_{\parallel}^2 H_z^2 \qquad \ldots (7)$$

and for $H \perp z$

$$H_s = D\{S_z^2 - \tfrac{1}{3}(S+1)S\} + \beta g_{\perp} H_x S_x - \beta^2 \alpha_{\perp} k_{\perp}^2 H_x^2 \qquad \ldots (8)$$

where

$$D = -(\alpha_{\parallel}\zeta_{\parallel}^2 - \alpha_{\perp}\zeta_{\perp}^2)$$

$$g_{\parallel} = 2(1 - k_{\parallel}\,\alpha_{\parallel}\,\zeta_{\parallel})$$

$$g_{\perp} = 2(1 - k_{\perp}\,\alpha_{\perp}\,\zeta_{\perp})$$

and

$$\alpha_{\parallel} = {}_{\parallel} \frac{(2a_0 + \sqrt{5}b_0)^2}{E_3 - E_0} \qquad \ldots (9)$$

$$\alpha_{\perp} = \frac{2\left(\sqrt{2}a_0 a_1 - \frac{1}{2}\sqrt{\frac{5}{2}}b_0 a_1 + \frac{3}{2\sqrt{2}}b_0 b_1\right)^2}{E_1 - E_0} + \frac{2\left(\sqrt{2}a_0 b_1 - \frac{1}{2}\sqrt{\frac{5}{2}}b_0 b_1 - \frac{3}{2\sqrt{2}}b_0 b_1\right)^2}{E'_3 - E'_0}$$

Here we have introduced the orbital reduction factors k_i and the spin orbit coupling coefficients $\zeta_i (i = \parallel \text{ or } \perp$ to the trigonal axis of the complex) reduced from the free ion value and rendered anisotropic due to covalency.

Operating with the spin Hamiltonian H_s (7) and (8) respectively upon the spin states $|1>, |0>, |-1>$ we derive the energy expressions as follows :

(a) $H \parallel z$

$$\left.\begin{aligned} W_1 &= \tfrac{1}{3}D + g_{\parallel}\beta H_z - \beta^2 k_{\parallel}^2 \alpha_{\parallel} H_z^2 \\ W_0 &= -\tfrac{2}{3}D - \beta^2 k_{\parallel}^2 \alpha_{\parallel} H_z^2 \\ W_{-1} &= \tfrac{1}{3}D - g_{\parallel}\beta H_z - \beta^2 k_{\parallel}^2 \alpha_{\parallel} H_z^2 \end{aligned}\right\}$$

(b) $H \perp z$

$$\left.\begin{aligned} W_1 &= \tfrac{1}{2}[-\tfrac{1}{3}D - 2\beta^2 k_{\perp}^2 \alpha_{\perp} H_x^2 + (D^2 + 4g_{\perp}\beta^2 H_x^2)^{\frac{1}{2}}] \\ W_0 &= \tfrac{1}{3}D - \beta^2 k_{\perp}^2 \alpha_{\perp} H_x^2 \\ W_{-1} &= \tfrac{1}{2}[-\tfrac{1}{3}D - 2\beta^2 k_{\perp}^2 \alpha_{\perp} H_x^2 - (D^2 + 4g_{\perp}^2\beta^2 H_x^2)^{\frac{1}{2}}] \end{aligned}\right\} \qquad \ldots (10)$$

The expression for the principal gm ionic magnetic susceptibility is given as usual by

$$K_i = -\left[\lim_{H \to 0} \left| \frac{N}{H} \frac{\sum_s \frac{\partial W_s^{(i)}}{\partial H} \exp\left(-\frac{W_s^{(i)}}{kT}\right)}{\sum_s \exp\left(-\frac{W_s^{(i)}}{kT}\right)} \right|_{(i = \parallel, \perp)} \right] \quad \ldots (11)$$

On substituting the values of $W_s^{(i)}$ obtained from (10) in the above expression one gets

$$K_{\parallel} = \frac{2N\beta^2 \left[\frac{g_{\parallel}^2}{kT} e^{-D/3kT} + 2\alpha_{\parallel} k_{\parallel}^2 e^{-D/3kT} + k_{\parallel}^2 \alpha_{\parallel} e^{2D/3kT}\right]}{2e^{-D/3kT} + e^{2D/3kT}}$$

and $\quad \ldots (12a)$

$$K_{\perp} = \frac{N\beta^2 \left[4k_{\perp}^2 \alpha_{\perp} e^{-D/3kT} + 2\alpha_{\perp} {}^2 k_{\perp} e^{2D/3kT} + \frac{2g_{\perp}^2}{D}\left(e^{2D/3kT} - e^{-D/3kT}\right)\right]}{2e^{-D/3kT} + e^{2D/3kT}}$$

On the assumption that $D << kT$ the exponentials can be expanded when (12a) reduces to (ignoring terms involving higher powers of D and $1/T^2$; see also Pryce, 1957)

$$K_{\parallel} = \frac{N\beta^2}{k}\left[2k\,\alpha_{\parallel} k_{\parallel}^2 + \frac{2g_{\parallel}^2}{3T} - \frac{2D\,g_{\parallel}^2}{9kT^2}\right]$$

$\quad \ldots (12b)$

$$K_{\perp} = \frac{N\beta^2}{k}\left[2k\alpha_{\perp} k_{\perp}^2 + \frac{2g_{\perp}^2}{3T} + \frac{Dg_{\perp}^2}{9kT^2}\right]$$

For the fluosilicate, since D is ~ 0.5 cm^{-1} at room temperature and ~ 0.1 cm^{-1} at 14°K (Penrose and Stevens, 1950), it is permissible to use eq. (12b); however, at temperatures of about 1°K, $D \sim kT$, and eq. (12a) is more proper to use. For the chlorostannate low temperature data are unavailable and (12b) is adequate for the present purposes.

Since these crystals have an anisotropy of less than 0.5% throughout the temperature range studied and since it has been directly measured in these experiments, it is more convenient to use the expression for the anisotropy

$$\Delta K = K_{\parallel} - K_{\perp}$$

and the mean susceptibility

$\bar{K} = \frac{1}{3}(K_{\|}+2K_{\perp})$. For $D << kT$ these reduce to

$$K = \frac{N\beta^2}{k}[\tfrac{2}{3}k(\alpha_{\|}k_{\|}^2+2\alpha_{\perp}k_{\perp}^2)+\frac{2\bar{g}^2}{3T}-\frac{2D}{9k\bar{T}^2}(g_{\|}^2-g_{\perp}$$

and

$$\Delta\bar{K} = \frac{N\beta^2}{k}[2k(\alpha_{\|}k_{\|}^2-\alpha_{\perp}k_{\perp}^2)+\frac{2}{3T}(g_{\|}^2-g_{\perp}^2)-\frac{D}{9k\bar{T}^2}(2g_{\|}^2+g \quad \ldots (13)$$

COMPARISON WITH EXPERIMENT

The theoretical parameters involved in the above expressions are the cubic field coefficient Dq, the second and fourth order trigonal field parameters A_2 and A_4, respectively, the orbital reduction factors k_i and the spin orbit coupling coefficients, ζ_i ($i = \|, \perp$). Recent experiments on the optical spectra of $NiSiF_6{\cdot}6H_2O$ (in 10% concentration in $ZnSiF_6{\cdot}6H_2O$) by Pryce *et al.* (1964) show a fairly broad band centered around 9,100 cm^{-1}, assigned to the transition $^3A_{2g} \rightarrow {}^3T_{2g}$ in the cubic field approximation, which is thus equal to $10Dq$. We have consequently accepted the values of Dq as 910 cm^{-1}, since the mean centre of the levels is expected to remain practically unaltered when a small trigonal component is superposed on the cubic levels.

E.s.r. data for $NiSiF_6{\cdot}6H_2O$ are reported by Holden, Kittel and Yager (1949) who find $g_{\|} = 2.36$ and $g = 2.29$ at the room temperature with $D = 0.50$ cm^{-1}, while Penrose and Stevens (1950) obtained, within experimental error, an isotropic g-value with D varying with temperature from 0.32 cm^{-1} at 200°K to 0.12 cm^{-1} at 14.6°K. Holden *et al.* ascribed the anisotropy in g-values to experimental errors.

In correlating the theory with experiment we have found by trial and error a set of values of α_i, k_i and ζ_i ($i = \|, \perp$) with $Dq = 910$ cm^{-1} which would give the best fit with the resonance D and g-values, as well as our susceptibility and anisotropy data. It was found that a much better agreement with experiment was obtained by taking D as $-ve$. In fitting the results for different temperatures k_i, ζ_i and Dq were assumed to remain constant with temperature, as these parameters are associated with strong bindings and hence are expected to change less with temperature. On the other hand, we have assumed that α_i (which is a function of Dq, A_2 and A_4 ; cf eq. 6 and 9) varies with temperature because of a greater likelihood of thermal changes in the anisotropic part of the ligand field, as also observed by earlier workers of this laboratory on many salts of the iron group (Bose *et al.*, 1957, 1958, 1961 et seq). The results are shown in Tables III and IV for the fluosilicate and the chlorostannate, respectively.

(a) *$NiSiF_6{\cdot}6H_2O$.*

It is seen from table III that the agreement between the calculated and observed values of g, D, $k_{\|}$ and $k_{\perp}$ with a suitable and reasonable choice of the parameters Dq, k_i and α_i ($i = //, \perp$) is very satisfactory particularly in view of the fact

TABLE III

Calculated ligand field parameters for $NiSiF_6 \cdot 6H_2O$

$Dq = 910\ cm^{-1}$; $k_{\|} = 0.786$; $k_{\perp} = 0.825$

$\zeta_{\|} = -295\ cm^{-1}$; $\zeta_{\perp} = -309.5\ cm^{-1}$

Temp. °K	$10^4\ \alpha_i$	g_i	$-D\ cm^{-1}$	$10^6 \cdot \Delta K$	$10^6 \overline{K}$
300	$\alpha_{\|} = 6.222$	$g_{\|} = 2.289$ (2.36)	0.50 (0.50)*	15.10 (14.82)	4556 (4534)
	$\alpha_{\perp} = 5.600$	$g_{\perp} = 2.286$* (2.29)			
200	$\alpha_{\|} = 6.159$	$g_{\|} = 2.286$ (2.29)†	0 29 (0 32)†	16.00 (16.23)	6720 (6684)
	$\alpha_{\perp} = 5.565$	$g_{\perp} = 2\ 284$ (2.29)			
140	$\alpha_{\|} = 6.025$	$g_{\|} = 2.279$	0.214	18.69 (18.57)	9466 (9456)
	$\alpha_{\perp} = 5.451$	$g_{\perp} = 2.278$			
90	$\alpha_{\|} = 5.982$	$g_{\|} = 2\ 277$ (2.26)	0 158 (0 17)†	25 90 (25.62)	14597 (14610)
	$\alpha = 5\ 418$	$g_{\perp} = 2.277$ (2.276)†			
14.6	$\alpha_{\|} = 4\ 705$	$g_{\|} = 2.218$	0.034 (0.12)†	136 (——)	84,250 (83,500)§
	$\alpha_{\perp} = 4.271$	$g_{\perp} = 2\ 218$			
1.54	$\alpha_{\|} = 3.450$	$g_{\|} = 2.160$	0.014	148 (——)	799,880 (800,000)§
	$\alpha_{\perp} = 3\ 133$	$g_{\perp} = 2.160$			

* E.s.r. data of Holden *et al.*, (1949).

† E.s.r. data of Penrose and Stevens (1950).

§ Moan susceptibility data of Haseda and Date (1958).

Figures within parentheses indicate experimental values.

that the anisotropy is very feeble. The change in D with temperature as observed by the resonance workers is also substantiated by these results, the calculated values being very close to the experimental ones obtained by e.s.r. We note here that the values of D calculated by Becquerel and Opechowsky (1939) based on the paramagnetic rotation data of Becquerel and van den Handel (1939) at 2°K is numerically higher ($D = -0.30\ cm^{-1}$) than the reasonance value ($D = -0.12\ cm^{-1}$) reported by Penrose and Stevens (1950), as well as that obtained by Benzie and Cooke (1950) from specific heat measurements at 0.95°K ($D = -0.15\ cm^{-1}$). This has been ascribed by Ollom and Van Vleck (1951) to the fact that the zero field splitting contains in it an appreciable contribution from exchange interaction between neighbouring paramagnetic ions while the calculations of

Becquerel and Opechowsky include only the crystal field contribution. Since we have chosen the value of D by trial so as to give the best fit with the experimental susceptibility and anisotropy data it should include both the above effects. The discrepancy between our calculated values and the e.s.r data below 14°K may arise from the fact that our value is not based on actual measurement of anisotropy at these temperatures but are the extrapolated ones to give close fit with the mean susceptibility data of Haseda and Date (1958). It has also been recently pointed out by Ohtsubo (1965) that exchange effects are small in $NiSiF_6 \cdot 6H_2O$ which becomes weakly ferromagnetic only below 0.15°K.

TABLE IV

Calculated ligand field parameters for $NiSnCl_6 \cdot 6H_2O$.

$D_q = 910\ cm^{-1}$

$k_{\|} = 0.760$ $\quad k_{\perp} = 0.757$

$\zeta_{\|} = -250.3\ cm^{-1}$ $\quad \zeta_{\perp} = -249.6\ cm^{-1}$

Temp. °K	$10^4\alpha_i$	g_i	$-D\ cm^{-1}$	$10^6\ K$	$10^6\ \bar{K}$
300	$\alpha_{\|} = 4.01$	$g_{\|} = 2.153$	0 52	18 78 (18 57)	3973 (3970)
	$\alpha_{\perp} = 3.95$	$g_{\perp} = 2\ 149$			
200	$\alpha_{\|} = 4.03$	$g_{\|} = 2.153$	0 52	31 61 (31.40)	5904 (5905)
	$\alpha_{\perp} = 3.97$	$g_{\perp} = 2.150$			
140	$\alpha_{\|} = 4.03$	$g_{\|} = 2.153$	0 52	50.52 (49 24)	8377 (8378)
	$\alpha_{\perp} = 3.97$	$g_{\perp} = 2.150$			
90	$\alpha_{\|} = 4.00$	$g_{\|} = 2\ 152$	0.40	75 59 (76.60)	12056 (12050)
	$\alpha_{\perp} = 3.96$	$g_{\perp} = 2.150$			

Figures within parentheses are experimental values.

It may be noted here that the contribution of D to the mean susceptibility, $\bar{K}$, (cf. eq. 13) is very small even at helium temperatures, while its effects on the anisotropy ΔK, becomes large at low temperatures. Hence anisotropy measurements are desirable at such temperatures for a more reliable estimate of D.

In is seen from eq. (4), (5) and (9) that α_i is a function of D_q, A_2 and A_4; hence it is possible to find the values of A_2 and A_4 (D_q being assumed to be constant) by trial to obtain agreement with the chosen value of α_i. Instead of calculating A_2 and A_4 for all the different sets of α's ($i = \|, \perp$) which would be very laborious and would not yield any new information we have estimated only

the order of magnitude of these parameters : $A_2 \sim -70$ cm^{-1} and $A_4 \sim 160$ cm^{-1} in the range 300°—90°K.

(b) *$NiSnCl_6 \cdot 6H_2O$.*

As mentioned earlier, the detailed x-ray structure of this crystal was performed by Pauling (1930). However, no magnetic susceptibility, e.s.r. or optical absorption data have yet been reported. Since the $Ni(H_2O)_6^{2+}$ octahedra in the fluosilicate and this salt are likely to be under very similar octahedral fields, we have assumed D_q to be the same in both. As before, we have found by trial a set of values of ζ_i, k_i and α_i which would give the best fit with the experimental susceptibility and anisotropy data while giving reasonable D and g-values (Table IV). We have also assumed, as before, D_q, k_i and ζ_i to be independent of temperature T, while α_i is assumed to vary with T.

As in the fluosilicate, it was found impossible to fit the experimental data with fixed values of $\alpha_{||}$ and $\alpha_\perp$ over the whole range of temperatures; however, the variation in these parameters, and consequently that of D and g_i is markedly less than those in the former salts. This points to a smaller change in the ligand field with temperature in the chlorostannate which may be due to greater strength of binding in this complex. It may be noted that both k_i and ζ_i have found to be smaller in this crystal than in the fluosilicate. This means a higher degree of covalency in the $Ni(H_2O)_6^{2+}$ complex, presumably arising from the influence of the Cl^- ions, the next nearest neighbours of Ni^{2+} ; because of its larger size and hence a smaller charge density than in the F^- ions, it is expected to change inductively (Van Vleck, 1939) the metal-ligand charge overlap in the chlorostannate more than in the fluosilicate. Unfortunately, there are no resonance data to compare the calculated D and g-values in this case directly.

In the chlorostannate the value of A_2 was found to remain about the same as in the fluosilicate, while that of A_4 changed to ~ 90 cm^{-1}.

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